

FORM PTO-1350
(Rev. 12-29-99)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

022701-942

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.51)

09/913838

INTERNATIONAL APPLICATION NO.

PCT/FR00/00360

INTERNATIONAL FILING DATE

14 February 2000

PRIORITY DATE CLAIMED

18 February 1999

TITLE OF INVENTION
**METHOD FOR PREPARING LATEX BY EMULSION (CO)POLYMERISATION OF ETHYLENICALLY
UNSATURATED MONOMERS, WITH DIRECT INLINE MONITORING BY RAMAN SPECTROSCOPY**
APPLICANT(S) FOR DO/EO/US
Mathias AGNELY; Bruno AMRAM; Phil D. ARMITAGE; Dominique CHARMOT; Bruno DROCHON; Eve PERE

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
 2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
 3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and the PCT Articles 22 and 39(1).
 4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
 5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
 6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
 7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
 8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
 9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
 10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:**
11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
 12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
 13. ☒ A FIRST preliminary amendment.
 ☐ A SECOND or SUBSEQUENT preliminary amendment.
 14. ☐ A substitute specification.
 15. ☐ A change of power of attorney and/or address letter.
 16. ☐ Other items or information:

U.S. APPLICATION NO. 09/913838

INTERNATIONAL APPLICATION NO.
PCT/FR00/00360ATTORNEY'S DOCKET NUMBER
022701-94217. ☒ The following fees are submitted:

CALCULATIONS

PTO USE ONLY

Basic National Fee (37 CFR 1.492(a)(1)-(5)):

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1,000.00 (960)

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 (970)

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 (958)

International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 (956)

International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 (962)

ENTER APPROPRIATE BASIC FEE AMOUNT =

\$ 860.00

Surcharge of \$130.00 (154) for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(e)). 20 ☐ 30 ☐

\$

Claims	Number Filed	Number Extra	Rate
Total Claims	17 -20 =	0	X\$18.00 (966)
Independent Claims	1 -3 =	0	X\$80.00 (964)
Multiple dependent claim(s) (if applicable)			+ \$270.00 (968)

\$

TOTAL OF ABOVE CALCULATIONS =

\$ 860.00

Reduction for 1/2 for filing by small entity, if applicable (see below).

\$

SUBTOTAL =

\$ 860.00

Processing fee of \$130.00 (156) for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492(f)). 20 ☐ 30 ☐

\$

TOTAL NATIONAL FEE =

\$ 860.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 (581) per property +

\$

TOTAL FEES ENCLOSED =

\$ 860.00

Amount to be:

\$

charged

\$

a. ☐ Small entity status is hereby claimed.b. ☒ A check in the amount of \$ 860.00 to cover the above fees is enclosed.c. ☐ Please charge my Deposit Account No. 02-4800 in the amount of \$_____ to cover the above fees. A duplicate copy of this sheet is enclosed.d. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-4800. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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09/913838

518 Rec'd PCT/PTO 20 AUG 2001

Patent
Attorney's Docket No. 022701-942

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of)
Mathias AGNELY et al.) Group Art Unit: (Unassigned)
Application No.: Unassigned) Examiner: (Unassigned)
(Corresponds to PCT/FR00/00360))
International Filing Date: 14 February 2000)
For: PROCESS FOR THE PREPARATION)
OF A LATEX BY EMULSION)
(CO)POLYMERIZATION OF)
ETHYLENICALLY UNSATURATED)
MONOMERS WITH DIRECT IN-LINE)
MONITORING BY RAMAN)
SPECTROSCOPY)

PRELIMINARY AMENDMENT

BOX PCT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination, please amend the above-captioned application as follows:

IN THE CLAIMS:

Kindly replace claims 1-17 as follows:

1. (Amended) A process for the preparation of a latex with predefined properties by emulsion (co)polymerization of at least one kind of ethylenically unsaturated monomer, wherein the process is carried out with continuous *in situ* monitoring of the (co)polymerization comprising the following stages:
 - (i) emitting incident light radiation within the spectral band situated between 200 nm and 1 400 nm, into the emulsion,

(ii) picking up the light scattered by the reaction medium and transmitting it to a Raman spectrometer,

(iii) determining the Raman spectrum, which shows the energy of the scattered light as a function of the difference in wavelength with respect to the incident light radiation,

(iv)

a) by either the intensities (areas or heights) of specific lines of the spectrum:

- of un(co)polymerized free monomer(s) in the reaction medium,
- and of the polymer obtained,

b) or the concentrations of un(co)polymerized free monomer(s) in the reaction medium and of the polymer obtained are calculated from the Raman spectrum using quantitative spectral analytical methods;

(v) calculating the process data either from the concentrations of free monomer(s) and of the polymer obtained or from the intensities (areas or heights) of specific lines of the spectrum of free monomer(s) in the reaction medium and from the intensities (areas or heights) of specific lines of the spectrum of the polymer obtained;

(vi) comparing these process data with reference data specific to the process for the production of the latex with the predefined properties;

(vii) and adjusting the reaction parameters, comprising the pressure, the stirring of the medium and the feeding with monomers, in order to minimize the difference between the process data measured in-line and the reference process data.

2. (Amended) The process as claimed in claim 1, wherein the Raman spectrometer is a Fourier transform or optical dispersive Raman spectrometer.

3. (Amended) The process as claimed in claim 2, wherein the latex results from the emulsion (co)polymerization of ethylenically unsaturated monomers selected from the group consisting:

- of styrene and/or its derivatives;
- of dienes;
- of (meth)acrylic esters comprising esters of acrylic acid and of methacrylic acid with hydrogenated or fluorinated C₁-C₁₂;
- of vinyl nitriles having from 3 to 12 carbon atoms;
- of carboxylic acid vinyl esters;
- of vinyl halides;
- and their mixture.

4. (Amended) The process as claimed in claim 3, wherein the emulsion additionally comprises other ethylenically unsaturated monomers, (co)polymerizable with the monomers of the preceding claim, selected from the group consisting of:

- unsaturated ethylenic mono- and dicarboxylic acids;
- monoalkyl esters of the abovementioned dicarboxylic acids with alkanols and their N-substituted derivatives;
- amides of unsaturated carboxylic acids;

- ethylenic monomers comprising a sulfonic acid group and its alkali metal or ammonium salts;

- unsaturated ethylenic monomers comprising a secondary, tertiary or quaternary amino group or a heterocyclic group comprising nitrogen;

- zwitterionic monomers;

- and their mixture.

5. (Amended) The process as claimed in claim 4, wherein the direct in-line monitoring is carried out continuously for the preparation of styrene/butadiene latex by the aqueous emulsion (co)polymerization of styrene with butadiene.

6. (Amended) The process as claimed in claim 1, wherein the direct in-line monitoring is carried out for the preparation of a latex by emulsion (co)polymerization in which the continuous phase is composed of water.

7. (Amended) The process as claimed in claim 1, wherein the intensity (area or height) of the specific lines of the Raman scattering spectrum is calculated:

- on the one hand, at approximately $1\,635 \pm 100\text{ cm}^{-1}$, a line associated with the stretching vibration of the carbon-carbon double bond of the free monomers which have not yet (co)polymerized,

- and, on the other hand, at approximately $1\,660 \pm 100\text{ cm}^{-1}$, a line associated with the stretching vibrations of the carbon-carbon double bonds incorporated in the main

chain of the polymer obtained when the monomer mixture comprises at least one dicne compound.

8. (Amended) The process as claimed in claim 1, wherein the direct in-line monitoring is carried out by calculating the concentrations of free monomer(s) and of the polymer obtained by multivariable chemometric analytical methods, this calculation being made by a computer having in memory equations establishing a correlation between the Raman spectra and the concentrations of free monomer(s) and of the polymer obtained and the measured Raman spectra being introduced into said memory in order to calculate the concentrations of free monomer(s) and of the polymer obtained during the polymerization.

9. (Amended) A latex-based composition capable of being obtained by the emulsion (co)polymerization process as claimed in claim 1.

10. (Amended) A device for the direct in-line monitoring *in situ* of the process for the preparation of a latex with predefined properties by emulsion (co)polymerization of ethylenically unsaturated monomers as claimed in claim 1, comprising:

- (i) a reactor comprising at least one means for feeding with monomers, with surfactants, with (co)polymerization initiator and with water;
- (ii) at least one optical probe which makes it possible to analyze the contents of the reactor;
- (iii) a Raman spectrometer;

(iv) at least one optical fiber

- via which fiber incident light radiation with a wavelength of between 200 nm and 1 400 nm, is conveyed from the Raman spectrometer to the optical probe,
- and via which fiber the light scattered by the reaction medium is reconveyed to the spectrometer providing the Raman spectrum, the optical fiber being identical or different for the conveying and the reconveying;

(v) a calculator, coupled to the spectrometer, making it possible to calculate, from the Raman spectrum:

- a) either the intensities (areas or heights) of specific lines of the spectrum
 - of un(co)polymerized free monomer(s) in the reaction medium
 - and of the polymer obtained,
- b) or the concentrations of un(co)polymerized free monomer(s) in the reaction medium and of the polymer obtained, from the Raman spectrum using quantitative spectral analytical methods;

(vi) and an adjusting automaton in which is programmed at least one mathematical algorithm making it possible to adjust the reaction parameters comprising the temperature, the pressure, the rate of stirring of the medium and the feeding with monomers, in order to minimize the difference between the process data measured in-line and the reference process data; the process data being based on an algebraic transformation either of the line intensities or of the concentrations of free monomer(s) and of the polymer obtained, and the reference data), based on this same algebraic transformation, being specific data of the process for the production of the latex with predefined properties.

11. (Amended) The device as claimed in claim 1, wherein the adjusting automaton is a programable device comprising at least one mathematical algorithm, said device being in contact with the calculator coupled to the Raman spectrometer, makes it possible to act continuously on the parameters of the process to reproduce a predetermined instantaneous conversion profile.

12. (Amended) The device as claimed in claim 10, wherein the Raman spectrometer is a Fourier transform Raman spectrometer and comprises a light radiation source, an interferometric optical system, a detector, an electronic system and a computing system.

13. (Amended) The device as claimed in claim 10, wherein the optical probe is directly positioned close to the reactor in which the (co)polymerization takes place, without distinction

- either in contact with the reaction medium,
- or placed behind a window, so that there is no physical contact between said probe and the reaction medium.

14. (Amended) The device as claimed in claim 10, wherein the probe comprises one or more means intended to weaken and/or to remove the interfering spectrum or spectra.

15. (Amended) The device as claimed in claim 14, wherein the probe comprises a first means intended to remove the Raman spectrum produced by the optical fiber transporting the incident irradiation and a second means intended to weaken the Rayleigh scattering of the probed molecules.

16. (Amended) The device as claimed in claim 10, wherein the first and second means are optical filters selected from the group consisting of holographic filters, dielectric filters and dichroic filters.

17. (Amended) The device as claimed in claim 10, wherein the transmission of the incident radiation and scattered radiation takes place via optical fibers comprising individual and separate inlet and outlet ports.

REMARKS

Entry of the foregoing amendment(s) is respectfully requested.

The claims have been amended to eliminate multiple dependency and to place them in better condition for U.S. patent practice.

Should the Examiner have any questions concerning the subject application, a telephone call to the undersigned would be appreciated.

Respectfully submitted,

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By: 

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Date: August 20, 2001

Attachment to Preliminary Amendment dated August 20, 2001

Marked-up Claims 1-17

1. (Amended) A process for the preparation of a latex with predefined properties by emulsion (co)polymerization of at least one kind of ethylenically unsaturated monomer, [characterized in that] wherein the process is carried out with continuous *in situ* monitoring of the (co)polymerization comprising the following stages:

(i) ~~emitting~~ incident light radiation within the spectral band situated between 200 nm and 1 400 nm, [and preferably between 700 nm and 1 400 nm, is emitted] into the emulsion,

(ii) ~~picking up~~ the light scattered by the reaction medium [is picked up and transmitted] ~~and transmitting it~~ to a Raman spectrometer,

(iii) ~~determining~~ the Raman spectrum, which shows the energy of the scattered light as a function of the difference in wavelength with respect to the incident light radiation[, is determined],

(iv)

a) by either the intensities (areas or heights) of specific lines of the spectrum:

- of un(co)polymerized free monomer(s) in the reaction medium,
- and of the polymer obtained,

b) or the concentrations of un(co)polymerized free monomer(s) in the reaction medium and of the polymer obtained are calculated from the Raman spectrum using quantitative spectral analytical methods[, these methods preferably being multivariable chemometric methods];

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Marked-up Claims 1-17

(v) calculating the process data [are calculated] either from the concentrations of free monomer(s) and of the polymer obtained or from the intensities (areas or heights) of specific lines of the spectrum of free monomer(s) in the reaction medium and from the intensities (areas or heights) of specific lines of the spectrum of the polymer obtained;

(vi) comparing these process data [are compared] with reference data specific to the process for the production of the latex with the predefined properties;

(vii) and adjusting the reaction parameters, [such as the temperature,] comprising the pressure, the stirring of the medium and the feeding with monomers, [are adjusted] in order to minimize the difference between the process data measured in-line and the reference process data.

2. (Amended) The process as claimed in claim 1, [characterized in that] wherein the Raman spectrometer is a Fourier transform or optical dispersive Raman spectrometer[, preferably a Fourier transform Raman (FT-Raman) spectrometer].

3. (Amended) The process as claimed in [the preceding] claim 2, [characterized in that] wherein the latex results from the emulsion (co)polymerization of ethylenically unsaturated monomers [chosen] selected from the group consisting:

- of styrene and/or its derivatives[, in particular derivatives such as α -methylstyrene or vinyltoluene];
- of dienes[, such as butadiene, isoprene or 2-chloro-1,3-butadiene];

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Marked-up Claims 1-17

- of (meth)acrylic esters[, this term denoting] comprising esters of acrylic acid and of methacrylic acid with hydrogenated or fluorinated C₁-C₁₂[, preferably C₁-C₈, alcohols, in particular methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, tertbutyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate or isobutyl methacrylate];

- of vinyl nitrites[, preferably those] having from 3 to 12 carbon atoms[, such as acrylonitrile and methacrylonitrile];

- of carboxylic acid vinyl esters[, such as vinyl acetate, vinyl versatate or vinyl propionate];

- of vinyl halides;

- and their mixture.

4. (Amended) The process as claimed in [the preceding] claim 3, [characterized in that] wherein the emulsion additionally comprises other ethylenically unsaturated monomers, (co)polymerizable with the monomers of the preceding claim, [chosen] selected from the group consisting of:

- unsaturated ethylenic mono- and dicarboxylic acids[, such as acrylic acid, methacrylic acid, itaconic acid, maleic acid or fumaric acid];

- monoalkyl esters of the abovementioned dicarboxylic acids with alkanols[, preferably having from 1 to 4 carbon atoms,] and their N-substituted derivatives;

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Marked-up Claims 1-17

- amides of unsaturated carboxylic acids[, such as acrylamide, methacrylamide, N-methylolacrylamide, methacrylamide and N-alkylacrylamides];
- ethylenic monomers comprising a sulfonic acid group and its alkali metal or ammonium salts[, such as vinylsulfonic acid, vinylbenzenesulfonic acid, α -acrylamidomethylpropanesulfonic acid or 2-sulfoethylene methacrylate];
- unsaturated ethylenic monomers comprising a secondary, tertiary or quaternary amino group or a heterocyclic group comprising nitrogen[, such as, for example, vinylpyridines, vinylimidazole, aminoalkyl (meth)acrylates and aminoalkyl(meth)acrylamides, such as dimethylaminoethyl acrylate or dimethylaminoethyl methacrylate, di(tert-butyl)aminoethyl acrylate or di(tert-butyl)aminoethyl methacrylate or dimethylaminomethylacrylamide or dimethylaminomethylmethacrylamide];
- zwitterionic monomers[, such as sulfopropyl(dimethyl)aminopropyl acrylate];
- and their mixture.

5. (Amended) The process as claimed in claim 4, [characterized in that] wherein the direct in-line monitoring is carried out continuously for the preparation of styrene/butadiene latex by the aqueous emulsion (co)polymerization of styrene with butadiene.

Attachment to Preliminary Amendment dated August 20, 2001

Marked-up Claims 1-17

6. (Amended) The process as claimed in [any one of the preceding claims] claim 1, [characterized in that] wherein the direct in-line monitoring is carried out for the preparation of a latex by emulsion (co)polymerization in which the continuous phase is composed of water.

7. (Amended) The process as claimed in [any one of the preceding claims] claim 1, [characterized in that] wherein the intensity (area or height) of the specific lines of the Raman scattering spectrum is calculated:

- on the one hand, at approximately $1\,635 \pm 100\text{ cm}^{-1}$, a line associated with the stretching vibration of the carbon-carbon double bond of the free monomers which have not yet (co)polymerized,

- and, on the other hand, at approximately $1\,660 \pm 100\text{ cm}^{-1}$, a line associated with the stretching vibrations of the carbon-carbon double bonds incorporated in the main chain of the polymer obtained when the monomer mixture comprises at least one diene compound.

8. (Amended) The process as claimed in [one of claims 1 to 6] claim 1, [characterized in that] wherein the direct in-line monitoring is carried out by calculating the concentrations of free monomer(s) and of the polymer obtained by multivariable chemometric analytical methods, this calculation being made by a computer having in memory equations establishing a correlation between the Raman spectra and the

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Marked-up Claims 1-17

concentrations of free monomer(s) and of the polymer obtained and the measured Raman spectra being introduced into said memory in order to calculate the concentrations of free monomer(s) and of the polymer obtained during the polymerization.

9. (Amended) A latex-based composition capable of being obtained by the emulsion (co)polymerization process as claimed in [any one of the preceding claims] claim 1.

10. (Amended) A device for the direct in-line monitoring *in situ* of the process for the preparation of a latex with predefined properties by emulsion (co)polymerization of ethylenically unsaturated monomers as claimed in [any one of claims 1 to 8] claim 1, comprising:

- (i) a reactor comprising at least one means for feeding with monomers, with surfactants, with (co)polymerization initiator and with water;
- (ii) at least one optical probe which makes it possible to analyze the contents of the reactor;
- (iii) a Raman spectrometer;
- (iv) at least one optical fiber
 - via which fiber incident light radiation with a wavelength of between 200 nm and 1 400 nm, [and preferably between 700 nm and 1 400 nm,] is conveyed from the Raman spectrometer to the optical probe,

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Marked-up Claims 1-17

• and via which fiber the light scattered by the reaction medium is reconveyed to the spectrometer providing the Raman spectrum, the optical fiber being identical or different for the conveying and the reconveying;

(v) a calculator, coupled to the spectrometer, making it possible to calculate, from the Raman spectrum:

a) either the intensities (areas or heights) of specific lines of the spectrum

- of un(co)polymerized free monomer(s) in the reaction medium
- and of the polymer obtained,

b) or the concentrations of un(co)polymerized free monomer(s) in the reaction medium and of the polymer obtained, from the Raman spectrum using quantitative spectral analytical methods[, these methods preferably being multivariable chemometric methods];

(vi) and an adjusting automaton in which is [programed] **programmed** at least one mathematical algorithm making it possible to adjust the reaction parameters[, such as] **comprising** the temperature, the pressure, the rate of stirring of the medium and the feeding with monomers, in order to minimize the difference between the process data measured in-line and the reference process data; the process data being based on an algebraic transformation either of the line intensities or of the concentrations of free monomer(s) and of the polymer obtained, and the reference data), based on this same algebraic transformation, being specific data of the process for the production of the latex with predefined properties.

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Marked-up Claims 1-17

11. (Amended) The device as claimed in [the preceding] claim 1, [characterized in that] wherein the adjusting automaton is a programable device comprising at least one mathematical algorithm, said device being in contact with the calculator coupled to the Raman spectrometer, makes it possible to act continuously on the parameters of the process to reproduce a predetermined instantaneous conversion profile.

12. (Amended) The device as claimed in [either one of claims 10 and 11] claim 10, [characterized in that] wherein the Raman spectrometer is a Fourier transform Raman spectrometer and comprises a light radiation source, an interferometric optical system, a detector, an electronic system and a computing system.

13. (Amended) The device as claimed in [any one of claims 10 to 12] claim 10, [characterized in that] wherein the optical probe is directly positioned close to the reactor in which the (co)polymerization takes place, without distinction

- either in contact with the reaction medium,
- or placed behind a window, so that there is no physical contact between said probe and the reaction medium.

14. (Amended) The device as claimed in [any one of claims 10 to 13] claim 10, [characterized in that] wherein the probe comprises one or more means intended to weaken and/or to remove the interfering spectrum or spectra.

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Marked-up Claims 1-17

15. (Amended) The device as claimed in [the preceding] claim 14, [characterized in that] wherein the probe comprises a first means intended to remove the Raman spectrum produced by the optical fiber transporting the incident irradiation and a second means intended to weaken the Rayleigh scattering of the probed molecules.

16. (Amended) The device as claimed in [any one of claims 10 to 15] claim 10, [characterized in that] wherein the first and second means are optical filters [chosen in particular] selected from the group consisting of holographic filters, dielectric filters and dichroic filters.

17. (Amended) The device as claimed in [one of the preceding claims 10 to 16] claim 10, [characterized in that] wherein the transmission of the incident radiation and scattered radiation takes place via optical fibers comprising individual and separate inlet and outlet ports.

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518 Rec'd PCT/PTO 20 AUG 2001

WO 00/49395

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PCT/FR00/00360

PROCESS FOR THE PREPARATION OF A LATEX BY EMULSION
(CO)POLYMERIZATION OF ETHYLENICALLY UNSATURATED
MONOMERS WITH DIRECT IN-LINE MONITORING BY
RAMAN SPECTROSCOPY

5 A subject matter of the present invention is
a novel process for the preparation of a latex by
emulsion (co)polymerization of ethylenically
unsaturated monomers, in which the direct in-line
monitoring of the (co)polymerization is carried out by
10 Raman spectroscopy.

The latex-based compositions capable of being
obtained by the emulsion (co)polymerization process,
the in-line monitoring of which is carried out by Raman
spectroscopy, constitute the second subject matter of
15 the invention.

Finally, the third subject matter of the
invention relates to a device for the implementation of
the abovementioned process, this device comprising a
reactor, at least one optical probe, a Raman
20 spectrometer, optical fibers, a calculator and an
adjusting automaton.

Latex-based compositions are used in numerous
industries, in particular in those of paints, coatings,
adhesives, textiles and paper coating. Among latex
25 preparation processes, emulsion (co)polymerization is
the most commonly used process.

The properties of the latex-forming

(co)polymer are closely related to its overall chemical composition but also to its macromolecular characteristics, such as the microstructure of the chains, the heterogeneity of their chemical composition, their molecular mass distribution and the fraction of optionally crosslinked (co)polymer. The necessary and desired properties are, of course, different according to the field of application of the latices. By way of examples, the desired properties are, for the coating of paper, the dry pick resistance, the wet pick resistance and the wrinkle resistance of the coated papers, for the coating of carpets, including fitted carpets, the mechanical strength and the flexibility, for adhesives, the adhesiveness and the shear strength, and for paints, the wet abrasion resistance, the blocking resistance and the film-forming temperature.

It is thus important to be able to employ a process for preparing a latex which makes it possible to obtain the latter with an overall chemical composition predefined in advance but also with predefined characteristics, in order to provide for and anticipate its future use in a field of application.

For this reason, the reproducibility of the process from one operation to another (batch to batch) is a key element in guaranteeing a consistent level of performance of the latex to the user of the latter. The

reproducibility of the process and the consistent quality of the latex obtained are guaranteed by following the process instructions and by identifying the critical parameters of the latter; use may be made, 5 for this, of a methodology, such as Statistical Process Control. In order for this to be all the more effective, it is necessary to be able to have available relevant indicators of the polymerization and preferably indicators which can be measured during the 10 process and not after the process, so as to be able to correct situations of drift. There thus exists a need to have available a technique for the in-line monitoring of the polymerization.

It is known to define the reaction parameters 15 of a process for the preparation of a latex by (co)polymerization in intending to obtain a latex with the appropriate properties in comparison with its use: for example, by defining the temperature profiles and the addition of the reactants, such as the monomers, 20 during the reaction. These reaction parameters thus defined generally result in a (co)polymerization rate profile which condition the characteristics of the latex obtained.

However, it is apparent that, at the 25 industrial level, observing the process parameters (temperature, feed profile of the monomers, pressure, and the like) does not guarantee absolute

reproducibility of said process and thus the production of a latex with predefined and appropriate qualities in comparison with their future use. This is because the reaction rate profile can be affected by other factors, such as the impurities present in the reactants [water, monomer(s), surfactant(s), and the like], the fluctuation in stirring rate, the surface condition of the reactant, the fluctuation in size of the particles, and the like.

Given the great economic and industrial stake with regard to the latices, there is very great advantage in having available an optimized emulsion (co)polymerization process for their preparation which guarantees to the user, above all, a consistent level of performance conferred by latices with predefined properties. Such a process must thus exhibit improved reproducibility.

To these ends, there has now been developed, and it is this which constitutes the first subject matter of the present invention, a novel optimized process for the preparation of a latex which exhibits improved reproducibility and, in addition, which is easy to implement, which has an acceptable manufacturing cost and which can be used on an industrial scale. This preparation process by emulsion (co)polymerization of at least one kind of ethylenically unsaturated monomer is carried out by

continuous *in situ* monitoring of the (co)polymerization comprising the following stages:

- (i) incident light radiation within the spectral band situated between 200 nm and 1 400 nm, and
5 preferably between 700 nm and 1 400 nm, is emitted into the emulsion,
- (ii) the light scattered by the reaction medium is picked up and transmitted to a Raman spectrometer,
- (iii) the Raman spectrum, which shows the energy of
10 the scattered light as a function of the difference in wavelength with respect to the incident light radiation, is determined,
- (iv)
 - a) either the intensities (areas or heights) of
15 specific lines of the spectrum:
 - of un(co)polymerized free monomer(s) in the reaction medium,
 - and of the polymer obtained;
 - b) or the concentrations of un(co)polymerized free
20 monomer(s) in the reaction medium and of the polymer obtained are calculated from the Raman spectrum using quantitative spectral analytical methods, these methods preferably being multivariable chemometric methods;
- 25 (v) the process data are subsequently calculated either from the concentrations of free monomer(s) and of the polymer obtained or from the intensities (areas

or heights) of specific lines of the spectrum of free monomer(s) in the reaction medium and of the polymer obtained;

- (vi) these process data are compared with
- 5 reference data specific to the process for the production of the latex with the predefined properties;
- (vii) and the reaction parameters, such as the temperature, the pressure, the stirring of the medium and the feeding with monomers, are adjusted in order to
- 10 minimize the difference between the process data measured in-line and the reference process data.

In the context of the present invention, the Raman spectrometer can be a Fourier transform Raman spectrometer or an optical dispersive Raman

- 15 spectrometer. According to a particular advantageous form, the spectrometer is a Fourier transform Raman (FT-Raman) spectrometer.

One of the advantageous characteristics of the process according to the invention is in particular

- 20 its continuous implementation, requiring no withdrawal and/or preparation of sample beforehand.

A second advantageous characteristic of the process according to the invention is the minimization of its sensitivity to possible local absences of

- 25 homogeneity in the medium within the reactor; this being due mainly to the simultaneous determination of the intensities of lines or of the concentrations of

free monomer(s) and of the polymer obtained.

A third advantageous characteristic of the invention is the complete suitability of the process according to the invention for direct in-line

5 monitoring carried out *in situ*.

The term "in-line monitoring" is understood to mean not only the direct in-line analysis of the (co)polymerization by recovery of process data calculated in real time and defined from the Raman

10 spectra but also the in-line adjustment, that is to say the adjustment of the reaction parameters according to the calculated data in order to optimize the process in order to obtain a latex with predetermined qualities appropriate for its future use.

15 More specifically, for a given latex which it is desired to obtain, this adjustment takes place in order to reduce the difference between the process data and reference data to a minimum and preferably to a value close to zero, these reference data being
20 determined beforehand and corresponding to those which are observed in the case where the process is optimized for the preparation of said latex with predetermined and desired qualities. For this, the reference data are selected from experimental trials resulting in the
25 latices with the desired properties. These reference data are determined by measurement on withdrawn samples in off-line analysis or preferably in on-line analysis.

These reference data subsequently make possible the establishment of a reference curve for said latex.

In other words, the direct in-line monitoring of the emulsion (co)polymerization by Raman spectroscopy reflects, first, through the spectra processed and converted into process data, the state of progress of the (co)polymerization at any instant. Then, secondly, simultaneously or virtually simultaneously, the direct in-line monitoring of the (co)polymerization by Raman spectroscopy makes possible the adjustment of the reaction parameters of the (co)polymerization process. Thus, the in-line monitoring makes it possible to improve the reproducibility of the (co)polymerization processes and to obtain latices with properties which are predetermined according to the desired objective.

The calculations of the process data and reference data can be made according to various methods. By way of example, the process data mentioned below can be monitored as a function of time:

- (a) the intensities of specific lines of the Raman spectrum (areas or heights) of the monomer(s) and of the polymer,
- (b) the concentration of monomer C_m and the concentration of polymer C_p ,
- (c) the ratio of the intensities of specific Raman lines (areas or heights) of the monomer(s) to the

intensities of specific Raman lines (areas or heights) of the polymer.

(d) the ratio of the monomer concentration to the polymer concentration C_m/C_p ,

5 (e) the instantaneous conversion, defined by

$$X_i = C_p / (C_p + C_m),$$

(f) the cumulative conversion, defined by

$X_c = C_p \times V_{tot}/M_{tot}$, where V_{tot} is the reaction volume of the latex and M_{tot} is the total monomer mass

10 involved in the process.

The units of these data are not important; however, they must be consistent with one another.

According to a preferred alternative form of the invention, the process data which make possible the
15 establishment of the reference curve are based on the instantaneous conversion X_i and the cumulative conversion X_c .

The reference data X_i^0 and X_c^0 , represented in the form of a curve $X_i^0 = F(X_c^0)$, are thus first
20 obtained from trials which have resulted in the characteristics desired for the purpose of the future application. In subsequent trials forming the subject of the direct in-line monitoring, the values of X_i and of X_c obtained in real time are compared with the
25 reference curve.

When a difference is observed between the calculated data X_i and X_c resulting from the process

and the reference data X_i^0 and X_c^0 , adjustment is carried out by corrective actions on the process reaction parameters in order to minimize this difference and, for this reason, to provide better reproducibility of said process for a given latex.

By way of example, in order to quantify the increase in reproducibility contributed by the in-line control of the polymerization, it is possible to measure the dispersion index (DI), which determines the difference of the process data X_i and X_c and the reference data X_i^0 and X_c^0 for a series of polymerization trials. This dispersion index, which characterizes the variability of the process, will be calculated by analyzing the data according to well known statistical methods, as described in Draper N.R., Smith H., 'Applied Regression Analysis', Second Edition, Wiley, 1981; Bates D.M., Watts D.G., 'Nonlinear Regression Analysis and its Applications', Wiley, 1988; and Tomassone R., Lesquoy E., Miller C., 'La Regression, Nouveaux Regards sur une Ancienne Méthode Statistique' [Regression, a New Look at a Long-Established Statistical Method], Masson, 1983.

The term "(co)polymerization" is understood to denote, for the purposes of the present invention, both the homopolymerization of ethylenically unsaturated monomers and their copolymerization.

Emulsion (co)polymerization denotes any

emulsion (co)polymerization process known to a person skilled in the art involving monomers as defined below in the presence of emulsifying agents and (co)polymerization initiators.

5 The nature of the emulsifying agents and initiators is not critical. The process according to the invention applies to any process for the emulsion (co)polymerization of ethylenically unsaturated monomers in the presence of the usual initiators and
10 emulsifying agents for these types of (co)polymerization.

 As regards the quantitative spectral analytical methods, they make it possible to measure the intensities (areas or heights) of specific lines of
15 the spectrum or to determine the concentrations of monomer(s) and of the polymer, preferably by using multivariable chemometric methods.

 For the direct intensity measurements on lines of the Raman spectrum, it is possible, by way of
20 examples, to measure the following respective areas or heights:

- on the one hand, at approximately
1 635 \pm 100 cm^{-1} , a line associated with the stretching vibration of the carbon-carbon double
25 bond of the free monomers which have not yet (co)polymerized,
- and, on the other hand, at approximately

1 660 \pm 100 cm⁻¹, a line associated with the stretching vibrations of the carbon-carbon double bonds incorporated in the main chain of the polymer when the monomer mixture comprises at least one diene compound.

The term "multivariable chemometric methods" is understood to mean the multivariable analytical techniques known to a person skilled in the art, such as:

- 10 - the partial least squares technique,
- the "neuronal network" analytical technique.

Reference may in particular be made on this subject to the document "Partial Least Squares Methods for Spectral Analyses" by Haaland D.M. and Thomas E.V.,
15 Anal. Chem., 1988, 60, 1193.

According to an advantageous alternative form of the invention, the direct in-line monitoring is carried out by calculating the concentrations of free monomer(s) and of the polymer obtained by multivariable
20 chemometric analytical methods, this calculation being made by a computer having in memory equations establishing a correlation between the Raman spectra and the concentrations of free monomer(s) and of the polymer obtained and the measured Raman spectra being
25 introduced into said memory in order to calculate the concentrations of free monomer(s) and of the polymer obtained during the polymerization.

In general, the frequency of the measurements recorded is tailored according to the rate of change of the process data. For example, the recordings are made at intervals of between 1 second and 30 minutes and
5 preferably between 10 seconds and 10 minutes.

Use is generally made, as ethylenically unsaturated monomers, of the monomers chosen from the group consisting:

- 10 - of styrene and/or its derivatives, in particular derivatives such as α -methylstyrene or vinyltoluene;
- of dienes, such as butadiene, isoprene or 2-chloro-1,3-butadiene;
- 15 - of (meth)acrylic esters, this term denoting esters of acrylic acid and of methacrylic acid with hydrogenated or fluorinated C_1 - C_{12} , preferably C_1 - C_8 , alcohols, in particular methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, tert-
20 butyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate or isobutyl methacrylate;
- of vinyl nitriles, preferably those having from 3 to 12 carbon atoms, such as acrylonitrile and
25 methacrylonitrile;
- of carboxylic acid vinyl esters, such as vinyl acetate, vinyl versatate or vinyl propionate;

- of vinyl halides;
- and their mixture.

Other ethylenically unsaturated monomers, alone or as mixtures, (co)polymerizable with the above

5 monomers are chosen from the group consisting of:

- unsaturated ethylenic mono- and dicarboxylic acids, such as acrylic acid, methacrylic acid, itaconic acid, maleic acid or fumaric acid;
- monoalkyl esters of the abovementioned
- 10 dicarboxylic acids with alkanols, preferably having from 1 to 4 carbon atoms, and their N-substituted derivatives;
- amides of unsaturated carboxylic acids, such as acrylamide, methacrylamide, N-methylolacrylamide,
- 15 methacrylamide and N-alkylacrylamides;
- ethylenic monomers comprising a sulfonic acid group and its alkali metal or ammonium salts, such as vinylsulfonic acid, vinylbenzenesulfonic acid, α -acrylamidomethylpropanesulfonic acid or
- 20 2-sulfoethylene methacrylate;
- unsaturated ethylenic monomers comprising a secondary, tertiary or quaternary amino group or a heterocyclic group comprising nitrogen, such as, for example, vinylpyridines, vinylimidazole,
- 25 aminoalkyl (meth)acrylates and aminoalkyl(meth)acrylamides, such as dimethylaminoethyl acrylate or dimethylaminoethyl

methacrylate, di(tert-butyl)aminoethyl acrylate or
di(tert-butyl)aminoethyl methacrylate or
dimethylaminomethylacrylamide or
dimethylaminomethylmethacrylamide;

- 5 - zwitterionic monomers, such as
sulfopropyl(dimethyl)aminopropyl acrylate;
- and their mixture.

According to an advantageous alternative form
of the invention, the direct in-line monitoring is
10 carried out by Fourier transform Raman spectroscopy and
relates to the aqueous emulsion (co)polymerization of
styrene and butadiene for the preparation of a latex of
styrene-butadiene type.

The invention also relates to a device for
15 the direct in-line monitoring *in situ* of the process
for the preparation of a latex with predefined
properties by emulsion (co)polymerization of
ethylenically unsaturated monomers. This device
according to the invention comprises:

- 20 (i) a reactor comprising at least one means for
feeding with monomers, with surfactants, with
(co)polymerization initiator and with water;
 (ii) at least one optical probe which makes it
possible to analyze the contents of the reactor;
25 (iii) a Raman spectrometer;
 (iv) at least one optical fiber
 • via which fiber incident light radiation

with a wavelength of between 200 nm and 1 400 nm, and preferably between 700 nm and 1 400 nm, is conveyed from the Raman spectrometer to the optical probe,

• and via which fiber the light scattered by the reaction medium is reconveyed to the spectrometer providing the Raman spectrum, the optical fiber being identical or different for the conveying and the reconveying;

(v) a calculator, coupled to the spectrometer, using quantitative spectral analytical methods making it possible to calculate, from the Raman spectrum:

a) either the intensities (areas or heights) of specific lines of the spectrum

- of un(co)polymerized free monomer(s) in the reaction medium
- and of the polymer obtained,

b) or the concentrations of un(co)polymerized free monomer(s) in the reaction medium and of the polymer obtained, from the Raman spectrum using quantitative spectral analytical methods, these methods preferably being multivariable chemometric methods;

(vi) and an adjusting automaton in which is programed at least one mathematical algorithm

making it possible to adjust the reaction parameters, such as the temperature, the pressure, the rate of stirring of the medium and the feeding with monomers, in order to minimize the difference between the process data measured in-line and the reference process data; the process data being based on an algebraic transformation either of the line intensities or of the concentrations of free monomer(s) and of the polymer obtained, and the reference data, based on this same algebraic transformation, being specific data of the process for the production of the latex with predefined properties.

The Raman spectrometer used is preferably a Fourier transform spectrometer (FT-Raman) and comprises a source of light radiation, an interferometric optical system, a detector, an electronic system and a computing system.

This spectrometer makes it possible to obtain Raman spectra which give the intensity of the scattered light as a function of the difference in wavelength with respect to the incident radiation.

More specifically, the Fourier transform spectrometer advantageously comprises:

- a source of light radiation intended to bring about light scattering by photon excitation of the molecules,

- an interferometric optical system which is used, inter alia, to screen out the Rayleigh scattering and to modulate the scatter signal, which modulation is carried out by virtue of the establishment of interferences between light radiation with two different values,
- a detector which converts light energy into electrical energy,
- an electronic system, the function of which is, inter alia, to convert the analog signal into a digital signal which can be used by the computing system,
- and a data processing system which is used, inter alia, to control the spectrometer, to carry out the data acquisition and to carry out the data processing, including in particular the inverse Fourier transform which provides the Raman spectrum.

The calculator, coupled to the spectrometer, carries out data processing employing measurements of the intensity (area or height) of certain specific lines of the Raman scattering spectrum or a chemometric analysis, preferably a multivariable chemometric analysis. This chemometric analysis makes it possible to determine both the concentrations of monomer(s) present and of the polymer. In the latter case, the calculator has in memory the equations establishing a

correlation between the Raman spectra obtained and the chemical composition of the latex in the course of polymerization. Thus, the measured Raman spectra are introduced into said memory and the chemical

- 5 composition of the latex in the course of polymerization is then calculated.

The calculator and the computing system of the Raman spectrometer can form two different and separate entities or a single entity.

- 10 The source of light radiation used for the incident irradiation is monochromatic. It is preferably a laser. Mention may be made, as examples of possible lasers, of an ionized argon laser (514.5 nm) or advantageously an Nd:YAG laser (1 064 nm). Generally,
15 the source of light radiation emits irradiation with a wavelength of between 200 nm and 1 400 nm, and preferably between 700 nm and 1 400 nm.

The optical probes for the analysis of the contents of the reactor can be found commercially.

- 20 Mention will be made, by way of example, of the Ramprobe probe from Bruker Optik (Germany). The analytical optical probe is directly positioned close to the reactor, without distinction either in contact with the reaction medium or placed behind a window, so
25 that there is no physical contact between said probe and the reaction medium.

However, it is recommended for the optical

probe to be positioned so that it is immersed from the beginning of the polymerization; under these conditions, the monitoring measurements made are representative of the process under way.

5 The optical probe positioned in the reactor is capable of withstanding the high pressures developed during polymerization and the negative pressures applied before polymerization for the purpose of removing oxygen from the reactor. In addition, the
10 probe must be completely leaktight in order to exclude any escape of gaseous monomer.

 Furthermore, the optical probe preferably comprises one or more means intended to weaken and/or to remove the interfering spectrum or spectra. These
15 means are in particular a first means intended to remove the Raman spectrum produced by the optical fiber transporting the incident irradiation and a second means intended to weaken the Rayleigh scattering of the probed molecules. In general, these means are optical
20 filters chosen in particular from holographic filters, dielectric filters and dichroic filters.

 The adjusting automaton is a programable device composed of at least one adjusting mathematic algorithm, said device being in contact with the
25 calculator coupled to the Raman spectrometer, makes it possible to act continuously on the parameters of the process to preferably reproduce a predetermined

instantaneous conversion profile.

Mention may be made, as examples of optical fibers which can be used in the context of the invention, of the fibers from CIC Photonics Inc., USA, 5 from C Technologies Inc., USA, from Sensotron Inc., USA and from Dow Corning, USA.

These fibers are usually silica fibers or fibers of any other material having a low effective Raman scattering cross section and a low optical 10 absorption in the wavelength range used.

In general, the optical fibers of the device according to the invention comprise individual and separate inlet and outlet ports by which the incident radiation and scattered radiation are transmitted.

15 The examples which follow are intended to illustrate the process and device according to the invention.

Examples

The examples below are carried out in a 20 pressure-resistant stainless steel reactor equipped with a stirrer of propeller type and with a baffle. Thermal adjustment is provided by a cryothermostat, which controls the temperature of a gilotherme fluid circulating in a jacket fitted around the reactor. The 25 reactants are introduced by means of membrane volumetric pumps; the flow rate of these reactants is controlled by directing the falling weight of cans

placed on balances.

The reaction parameters (reactant flow rates, temperature and pressure) are controlled by an adjusting automaton.

5 An FT-Raman probe (Ramprobe, Bruker Optik, Germany) is installed facing a window fitted through the jacket of the reactor, at the level of the blades of the stirrer. The window is made of quartz (Infrasil I, Heraeus, Germany).

10 A rubber seal prevents any stray light from interfering with the signal recorded by the probe and furthermore makes it possible to direct a stream of air in order to retain a temperature lower by 5 to 15°C than that in the reactor.

15 The probe is connected to a Fourier transform Raman spectrometer (RFS 100/S, Bruker Optik, Germany) via a first optical fiber (go direction) for transmission of the incident laser irradiation and via a second optical fiber (return direction) for
20 transmission of the Raman scattering.

The spectrometer is connected to a calculator in which the correlation equations and the algorithm for chemometric treatment of the Raman spectra are stored. The concentrations of the reactants (monomers,
25 polymers, water, and the like), determined by virtue of the multivariable chemometric analysis of the Raman spectra of the latex, are transmitted to the control

algorithm implanted in the adjusting automaton.

- Example 1:** Development of the method of in-line analysis from the Raman spectra, for the measurement of the concentration of free monomers and of the concentration of polymer obtained

The analytical method is established for a styrene/butadiene/acrylic acid emulsion polymerization reaction.

- 10 A. Procedure of the polymerization

The charges of reactants are shown in the table below.

Fraction	Ingredients	Mass (g)
	Water	1 600
	Sodium persulfate	12.1
A	Sodium hydrogen carbonate	11.5
	Sodium hydroxide	10.6
	Anionic surfactant	4.5
	Acrylic acid	63
	Butadiene	117
	Styrene	144
	Styrene	810
B	Butadiene	657
	tert-Dodecyl mercaptan	18
C	Sodium persulfate	6.5
	Water	150

- 15 Fraction A is charged, with the exception of

the styrene and butadiene, at a temperature of 30°C; after having purged the reactor with nitrogen, the styrene and butadiene mixture of fraction A is charged and the temperature is brought from 30°C to 75°C over 1 h. As soon as the temperature of 75°C is reached, fraction B is added over 6 h while controlling the temperature of the reactor at 75°C. The medium is maintained at this same temperature for an additional 6 h, during which fraction C is introduced. The reactor is subsequently cooled to ambient temperature and degassed.

B. Analysis of the polymerization

During the polymerization, samples of latex are withdrawn under pressure every 30 min and analyzed by gravimetry to determine the concentration of polymer C_p and by gas chromatography to determine the residual concentration of monomer C_m .

At the same time, Raman spectra are recorded every 6 min under the following conditions: 200 scans and a resolution of 8 cm^{-1} . They are stored in the calculator and then analyzed and compared with the concentrations data obtained off-line.

Chemometric software based on the PLS (Partial Least Squares) method makes it possible to obtain a set of correlation equations used to calibrate the analytical method.

C. Results

The concentrations of reactants are obtained with accuracy from the Raman spectra obtained, as is illustrated in figures 1 and 2:

- 5 - figure 1 [abscissa: concentration of styrene, measured by off-line chromatography (ppm/mass of latex); ordinate: concentration of styrene, predicted by the calibration (ppm/mass of latex)]
- 10 - and figure 2 [abscissa: concentration of polymer, measured by off-line gravimetry (mass%/mass of latex); ordinate: concentration of polymer, predicted by the calibration (mass%/mass of latex)].

15 Example 2: Validation of the in-line analytical methods of Example 1

A. Polymerization

The polymerization carried out in Example 1 is repeated in an identical fashion, except that the
20 level of persulfate is doubled.

B. In-line analysis of the polymerization

The Raman spectra recorded every 6 min are treated in-line in the calculator with the correlation equations determined in Example 1, so as to calculate
25 the concentrations of monomer(s) and of polymer. In the same way as in Example 1, samples are withdrawn off-line in order to analyze the concentrations of polymer

and of monomer(s).

C. Results

The concentrations as a function of time are given in figure 3 [abscissa: reaction time in min;

- 5 ordinate: white square: concentration of styrene, measured by off-line gas chromatography (ppm/mass of latex); black diamond: concentration of styrene, predicted by the calibration (ppm/mass of latex)].

- This example illustrates the ability of the
10 device to measure the concentration of reactants continuously from the Raman spectra acquired in-line, from the correlation equations established in Example 1.

- 15 Example 3: Measurement of the concentration of free monomers by the in-line analytical method of Example 1

A. Polymerization procedures

Example 3a:

- The charges of reactants are shown in the
20 table below. Fraction A is charged to the reactor at 30°C. The reactor is subsequently purged with nitrogen and its temperature is brought to 85°C over one hour. Fraction B is then introduced over 260 min and fraction C over 420 min.

- 25 Finally, the reactor is cooled to ambient temperature and degassed. The reactor is stirred at a speed of 175 revolutions/min throughout the duration of

the trial.

Fraction	Ingredients	Mass (g)
A	Water	1 600
	Latex with a solids content of 30%	23
	EDTA	0.4
	Acrylic acid	63
B	Styrene	1 152
	Butadiene	576
	tert-Dodecyl mercaptan	18
C	Water	250
	Sodium persulfate	18
	Anionic surfactant	10

Example 3b:

- 5 The procedure of Example 3b is identical to that of example 3a with the exception of the stirring speed, which is 225 revolutions/min.

Example 3c:

- 10 The procedure of example 3c is identical to that of example 3a with the exception of the stirring speed, which is 275 revolutions/min.

B. Analysis of the polymerizations

- (i) For these 3 examples 3a, 3b and 3c, the Raman spectra are recorded and processed in-line every 6 min
15 under the conditions described in example 2, so as to calculate the concentrations of monomer(s) and of polymer.

The calculations of concentration of styrene

with respect to time are given in figure 4.

The reaction time in min is on the abscissa. The white squares correspond to the concentrations of styrene in example 3a (ppm/mass of latex); the white diamonds are for the concentrations of styrene in example 3b (ppm/mass of latex); and the white circles represent the concentrations of styrene in example 3c (ppm/mass of latex)].

The concentration of polymer with respect to time is given in figure 5 [abscissa: reaction time in min; ordinate: white square: concentration of polymer in example 3a (mass%/mass of latex); white diamond: concentration of polymer in example 3b (mass%/mass of latex); white circle: concentration of polymer in Example 3c (mass%/mass of latex)].

(ii) At the same time, the pressure prevailing in the gaseous head space of the reactor is recorded for the 3 examples.

The pressures as a function of time are given in figure 6 for the first hour of polymerization [abscissa: reaction time in min; ordinate: white square: pressure during example 3a (bar); white diamond: pressure during example 3b (bar); white circle: pressure during example 3c (bar)].

The pressure in the gaseous head space is a qualitative indicator of the progress of the polymerization in the case of styrene/butadiene

lattices: it increases in proportion as the conversion falls.

C. Results

From figure 4, it is observed a priori that, during the first hour, the lower the stirring speed, the lower the concentration of free styrene. This would mean that the instantaneous conversion of the monomers increases in proportion as the stirring speed decreases.

However, this point is completely contradicted by the data in figure 6. This is because, in this figure, it is found that the pressure is not lower at the beginning of trial 3a than of trial 3c. The pressures are in fact virtually equivalent: which means that the conversion is therefore not greater during the first hour for example 3a.

This is furthermore confirmed by figure 5, in which are represented the variations in the concentration of polymer estimated from the Raman measurement for these same 3 trials, that is to say, the concentration of polymer, and thus also the conversion, is the same during the 3 trials in question.

These three examples thus show that, if the quality of the stirring is insufficient to provide for homogeneity in the reactor (for example, a portion of the monomers can float at the surface of the reaction

medium), the correct measurement of the concentration of monomer(s) is not possible. Thus, if only the measurement of the concentration of free monomer(s) is monitored, it is wrongly estimated that the

- 5 instantaneous conversion is high with respect to the reference data X_1^0 , which will result in erroneous corrective actions being taken in the event of adjustment. That is to say, the excessively fast or excessively slow introduction of fraction B, which does
- 10 not make it possible to guarantee the reproducibility of the process and the final quality of the latex.

Example 4: Measurement of the concentration of polymer obtained by the in-line analytical method of example 1

15 A. Polymerization procedures

Example 4a:

The polymerization procedure is identical to that of example 1.

Example 4b:

- 20 The polymerization procedure is identical to that of example 1. However, the pump which has to introduce fraction B, did not operate correctly during part of the polymerization (uneven flow rate).

The difference in behavior of the pump is

25 observed in figure 7 [abscissa: time (min); ordinate: white square: loss in weight (g) of the can containing fraction B during example 4a; black diamond: loss in

weight (g) of the can containing fraction B during example 4b. The loss in weight is steady in the case of example 4a, whereas oscillations are visible in the case of example 4b.

5 B. Analysis of the polymerizations

The Raman spectra recorded every 6 min are processed in-line in the calculator with the correlation equations determined in example 1, so as to calculate the concentrations of monomer(s) and of
10 polymer.

The calculations of the concentration of polymer as a function of time are given in figure 8 [abscissa: reaction time (min); ordinate: white square: concentration of polymer for example 4a (mass%/latex);
15 black diamond: concentration of polymer for example 4b (mass%/latex)].

The calculations of concentration of styrene as a function of time are given in figure 9 [abscissa: reaction time (min); ordinate: white square:
20 concentration of styrene during example 4a (ppm/latex); black diamond: concentration of styrene during example 4b (ppm/latex)].

C. Results

The curves of example 4a and of example 4b
25 are superimposed in figure 8.

The in-line measurement of the concentration of polymer in the latex thus does not reveal the

difference in the procedures of examples 4a and 4b (operation of the pump).

This measurement does not make it possible to anticipate the necessary corrections which make it possible to obtain identical latices in examples 4a and 4b. It can thus with difficulty by itself alone instantaneously report transitory events, such as inadequate temporary operation of a feed pump.

This example shows that the single in-line measurement of the concentration of polymer does not make it possible to guarantee the reproducibility of the process and the final quality of the latex.

Example 5: Simultaneous measurement of the concentration of free monomers and polymer obtained according to the method of example 1

A series of experiments, 5-1 to 5-10, is carried out by reproducing the polymerization procedure of example 1.

The in-line analysis of the concentration of monomer and of polymer is carried out under identical conditions to those of examples 2. The process data X_i (instantaneous conversion) and X_c (cumulative conversion) defined above, calculated from the concentrations C_m and C_p measured simultaneously in-line, are plotted in the curve $X_i = f(X_c)$ form.

10 curves corresponding to the 10

polymerization trials are thus obtained. The 10 curves differ by the experimental variability inherent to the process. The aim is to establish a confidence band around the reference curve from these 10 trials, which

- 5 will be known as the dispersion index (DI). The procedure for this is as follows: the reference curve is calculated by adjustment from the 10 experimental curves $X_i = f(X_c)$ of trials 5-1 to 5-10; it is thus a mean "reference" curve $X_i^0 = f(X_c^0)$.

- 10 The confidence band is constructed by calculating beforehand an estimation of the pure error from all the experimental results by applying the methodology described in the following work:
Draper N.R., Smith H., Applied Regression Analysis,
15 Second Edition, Wiley, 1981.

- The upper and lower limits of the simultaneous confidence band for the reference curve are thus calculated. The confidence level chosen is 99% (in other words, during polymerization, the value of
20 the process data at the instant under consideration lies within the confidence band, which means that the probability that the progress of the polymerization is not significantly different from that corresponding to the reference curve is greater than 0.99).

- 25 The dispersion index (DI) is the area of the confidence band calculated over the range defined by an abscissa (X_c) varying from 0 to 1 and an ordinate (X_i)

varying from 0 to 1. This crude value is multiplied by 1 000. The smaller the value of the DI, the less the process is dispersed and consequently the greater is the reproducibility and thus the reliability of this process. The calculations were carried out with the SAS/STAT and SAS/IML modules of the SAS software, version 6.12 (SAS Institute, USA). The results are given in the table below.

10 **Example 6. Process according to the invention:**
simultaneous in-line measurement of the concentration
of free monomers and polymer obtained according to the
method of example 1 and in-line adjustment

The series of trials 6-11 to 6-20 is carried
 15 out in an identical way to the series of example 5.
 However, fraction B is no longer introduced according to a predetermined profile; this is because a control algorithm is programed in the adjusting automaton to guide the feeding of the monomers of fraction B so as
 20 to minimize the error between the curve $X_i = f(X_c)$ and the preset curve $X_i^0 = f(X_c^0)$.

The control algorithm is based on adjustment of PID type ("proportional integral differential adjustment"). In the same way as for the series of
 25 trials 5-1 to 5-10, the statistical method presented above is used to calculate the confidence band over the 10 trials and to reduce therefrom the dispersion index

(DI). The results are given in the table below:

Reference of the trials	Dispersion index (DI)
5-1 to 5-10 (without in-line adjustment)	87
6-11 to 6-20 (<u>with</u> in-line adjustment)	50

Comparison of the series of trials of
5 example 5 and of the series of trials of example 6
reveals a much lower dispersion index (DI) when the
polymerization is carried out with in-line control
rendered possible by virtue of the in-line FT-Raman
analysis: the novel process forming the subject matter
10 of the invention is thus much more reproducible and,
for this reason, guarantees a consistent level of
performance.

CLAIMS

1. A process for the preparation of a latex with predefined properties by emulsion (co)polymerization of at least one kind of
- 5 ethylenically unsaturated monomer, characterized in that the process is carried out with continuous *in situ* monitoring of the (co)polymerization comprising the following stages:
- (i) incident light radiation within the spectral
- 10 band situated between 200 nm and 1 400 nm, and preferably between 700 nm and 1 400 nm, is emitted into the emulsion,
- (ii) the light scattered by the reaction medium is picked up and transmitted to a Raman spectrometer,
- 15 (iii) the Raman spectrum, which shows the energy of the scattered light as a function of the difference in wavelength with respect to the incident light radiation, is determined,
- (iv)
- 20 a) either the intensities (areas or heights) of specific lines of the spectrum:
- of un(co)polymerized free monomer(s) in the reaction medium,
 - and of the polymer obtained,
- 25 b) or the concentrations of un(co)polymerized free monomer(s) in the reaction medium and of the polymer obtained are calculated from the Raman

spectrum using quantitative spectral analytical methods, these methods preferably being multivariable chemometric methods;

- (v) the process data are calculated either from
5 the concentrations of free monomer(s) and of the polymer obtained or from the intensities (areas or heights) of specific lines of the spectrum of free monomer(s) in the reaction medium and from the intensities (areas or heights) of specific lines of the
10 spectrum of the polymer obtained;
- (vi) these process data are compared with reference data specific to the process for the production of the latex with the predefined properties;
- (vii) and the reaction parameters, such as the
15 temperature, the pressure, the stirring of the medium and the feeding with monomers, are adjusted in order to minimize the difference between the process data measured in-line and the reference process data.

2. The process as claimed in claim 1,
20 characterized in that the Raman spectrometer is a Fourier transform or optical dispersive Raman spectrometer, preferably a Fourier transform Raman (FT-Raman) spectrometer.

3. The process as claimed in the preceding
25 claim, characterized in that the latex results from the emulsion (co)polymerization of ethylenically unsaturated monomers chosen from the group consisting:

- of styrene and/or its derivatives, in particular derivatives such as α -methylstyrene or vinyltoluene;
- of dienes, such as butadiene, isoprene or
5 2-chloro-1,3-butadiene;
- of (meth)acrylic esters, this term denoting esters of acrylic acid and of methacrylic acid with hydrogenated or fluorinated C_1 - C_{12} , preferably C_1 - C_8 , alcohols, in particular methyl acrylate,
10 ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, tert-butyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate or isobutyl methacrylate;
- 15 - of vinyl nitriles, preferably those having from 3 to 12 carbon atoms, such as acrylonitrile and methacrylonitrile;
- of carboxylic acid vinyl esters, such as vinyl acetate, vinyl versatate or vinyl propionate;
- 20 - of vinyl halides;
- and their mixture.

4. The process as claimed in the preceding claim, characterized in that the emulsion additionally comprises other ethylenically unsaturated monomers,
25 (co)polymerizable with the monomers of the preceding claim, chosen from the group consisting of:

- unsaturated ethylenic mono- and dicarboxylic

- acids, such as acrylic acid, methacrylic acid, itaconic acid, maleic acid or fumaric acid;
- monoalkyl esters of the abovementioned dicarboxylic acids with alkanols, preferably having from 1 to 4 carbon atoms, and their N-substituted derivatives;
- amides of unsaturated carboxylic acids, such as acrylamide, methacrylamide, N-methylolacrylamide, methacrylamide and N-alkylacrylamides;
- ethylenic monomers comprising a sulfonic acid group and its alkali metal or ammonium salts, such as vinylsulfonic acid, vinylbenzenesulfonic acid, α -acrylamidomethylpropanesulfonic acid or 2-sulfoethylene methacrylate;
- unsaturated ethylenic monomers comprising a secondary, tertiary or quaternary amino group or a heterocyclic group comprising nitrogen, such as, for example, vinylpyridines, vinylimidazole, aminoalkyl (meth)acrylates and aminoalkyl(meth)acrylamides, such as dimethylaminoethyl acrylate or dimethylaminoethyl methacrylate, di(tert-butyl)aminoethyl acrylate or di(tert-butyl)aminoethyl methacrylate or dimethylaminomethylacrylamide or dimethylaminomethylmethacrylamide;
- zwitterionic monomers, such as sulfopropyl(dimethyl)aminopropyl acrylate;

- and their mixture.

5 5. The process as claimed in claim 4,
characterized in that the direct in-line monitoring is
carried out continuously for the preparation of
15 styrene/butadiene latex by the aqueous emulsion
(co)polymerization of styrene with butadiene.

6. The process as claimed in any one of the
preceding claims, characterized in that the direct in-
line monitoring is carried out for the preparation of a
10 latex by emulsion (co)polymerization in which the
continuous phase is composed of water.

7. The process as claimed in any one of the
preceding claims, characterized in that the intensity
(area or height) of the specific lines of the Raman
15 scattering spectrum is calculated:

- on the one hand, at approximately
1 635 \pm 100 cm^{-1} , a line associated with the
stretching vibration of the carbon-carbon double
bond of the free monomers which have not yet
20 (co)polymerized,
- and, on the other hand, at approximately
1 660 \pm 100 cm^{-1} , a line associated with the
stretching vibrations of the carbon-carbon double
bonds incorporated in the main chain of the
25 polymer obtained when the monomer mixture
comprises at least one diene compound.

8. The process as claimed in one of

claims 1 to 6, characterized in that the direct in-line monitoring is carried out by calculating the concentrations of free monomer(s) and of the polymer obtained by multivariable chemometric analytical methods, this calculation being made by a computer having in memory equations establishing a correlation between the Raman spectra and the concentrations of free monomer(s) and of the polymer obtained and the measured Raman spectra being introduced into said memory in order to calculate the concentrations of free monomer(s) and of the polymer obtained during the polymerization.

9. A latex-based composition capable of being obtained by the emulsion (co)polymerization process as claimed in any one of the preceding claims.

10. A device for the direct in-line monitoring *in situ* of the process for the preparation of a latex with predefined properties by emulsion (co)polymerization of ethylenically unsaturated monomers as claimed in any one of claims 1 to 8, comprising:

- (i) a reactor comprising at least one means for feeding with monomers, with surfactants, with (co)polymerization initiator and with water;
- (ii) at least one optical probe which makes it possible to analyze the contents of the reactor;
- (iii) a Raman spectrometer;

(iv) at least one optical fiber

- via which fiber incident light radiation with a wavelength of between 200 nm and 1 400 nm, and preferably between 700 nm and 1 400 nm, is conveyed from the Raman spectrometer to the optical probe,

- and via which fiber the light scattered by the reaction medium is reconveyed to the spectrometer providing the Raman spectrum, the optical fiber being identical or different for the conveying and the reconveying;

(v) a calculator, coupled to the spectrometer, making it possible to calculate, from the Raman spectrum:

a) either the intensities (areas or heights) of specific lines of the spectrum

- of un(co)polymerized free monomer(s) in the reaction medium
- and of the polymer obtained,

b) or the concentrations of un(co)polymerized free monomer(s) in the reaction medium and of the polymer obtained, from the Raman spectrum using quantitative spectral analytical methods, these methods preferably being multivariable chemometric methods;

(vi) and an adjusting automaton in which is

programed at least one mathematical algorithm making it possible to adjust the reaction parameters, such as the temperature, the pressure, the rate of stirring of the medium and the feeding with monomers, in order to minimize the difference between the process data measured in-line and the reference process data; the process data being based on an algebraic transformation either of the line intensities or of the concentrations of free monomer(s) and of the polymer obtained, and the reference data), based on this same algebraic transformation, being specific data of the process for the production of the latex with predefined properties.

11. The device as claimed in the preceding claim, characterized in that the adjusting automaton is a programable device comprising at least one mathematical algorithm, said device being in contact with the calculator coupled to the Raman spectrometer, makes it possible to act continuously on the parameters of the process to reproduce a predetermined instantaneous conversion profile.

12. The device as claimed in either one of claims 10 and 11, characterized in that the Raman spectrometer is a Fourier transform Raman spectrometer and comprises a light radiation source, an interferometric optical system, a detector, an

electronic system and a computing system.

13. The device as claimed in any one of claims 10 to 12, characterized in that the optical probe is directly positioned close to the reactor in which the (co)polymerization takes place, without distinction

- either in contact with the reaction medium,
- or placed behind a window, so that there is no physical contact between said probe and the reaction medium.

14. The device as claimed in any one of claims 10 to 13, characterized in that the probe comprises one or more means intended to weaken and/or to remove the interfering spectrum or spectra.

15. The device as claimed in the preceding claim, characterized in that the probe comprises a first means intended to remove the Raman spectrum produced by the optical fiber transporting the incident irradiation and a second means intended to weaken the Rayleigh scattering of the probed molecules.

16. The device as claimed in any one of claims 10 to 15, characterized in that the first and second means are optical filters chosen in particular from holographic filters, dielectric filters and dichroic filters.

17. The device as claimed in one of the preceding claims 10 to 16, characterized in that the

transmission of the incident radiation and scattered radiation takes place via optical fibers comprising individual and separate inlet and outlet ports.

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Figure 1

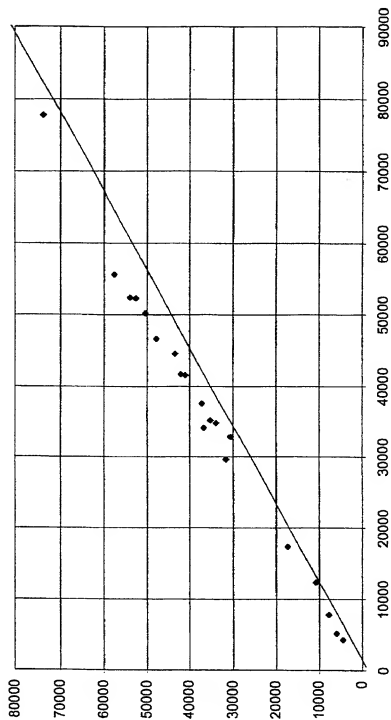


Figure 2

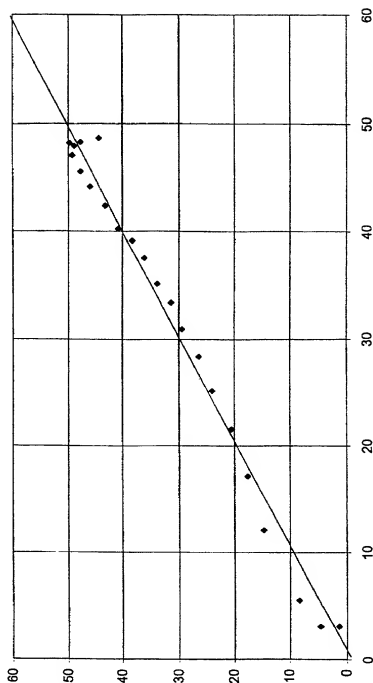


Figure 3

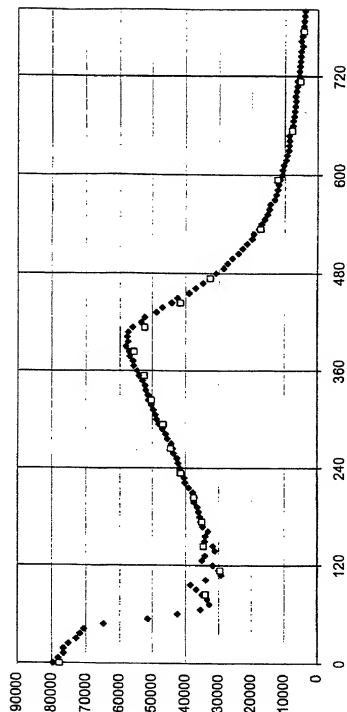


Figure 4

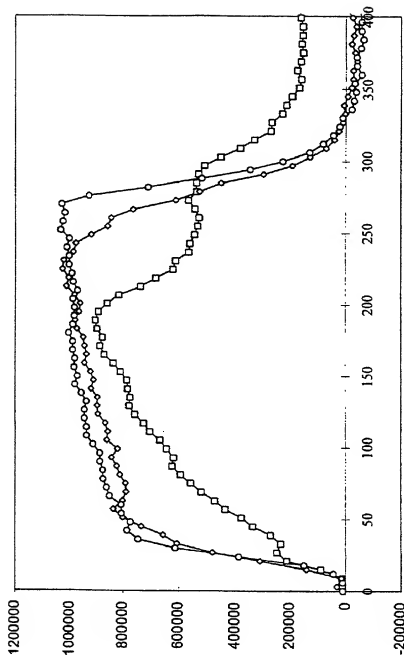
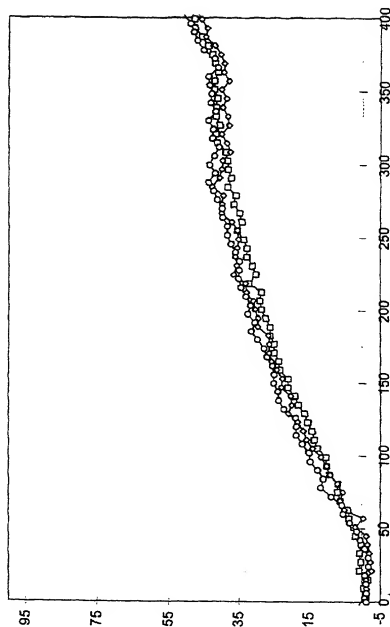


Figure 5



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Figure 6

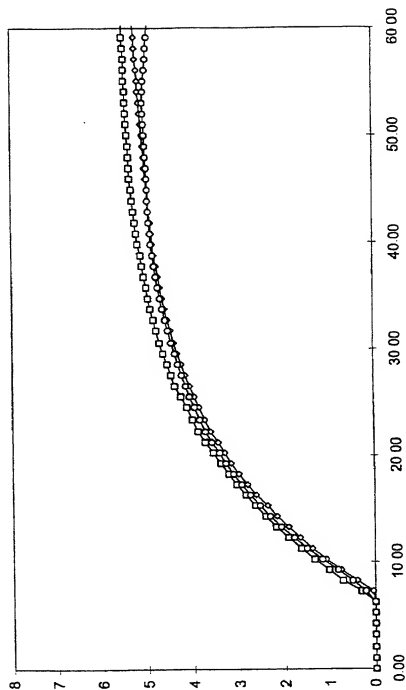
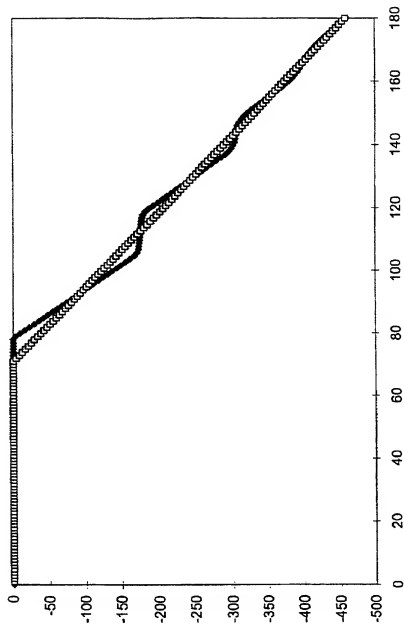
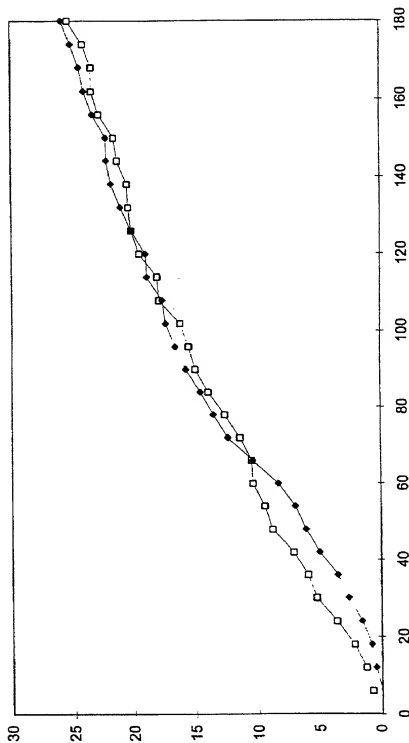


Figure 7



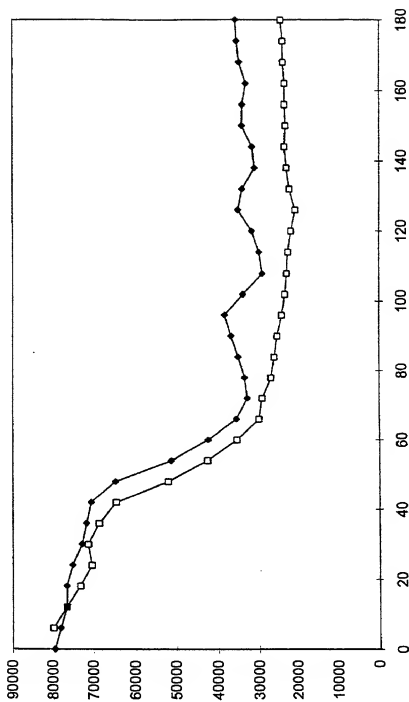
B/9

Figure 8



9/9

Figure 9



#4

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
 (Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

022701-942

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;
 I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor
 (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention
 entitled:

METHOD FOR PREPARING LATEX BY EMULSION (CO)POLYMERISATION OF ETHYLENICALLY
UNSATURATED MONOMERS, WITH DIRECT INLINE MONITORING BY RAMAN SPECTROSCOPY

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Number _____

on _____

and was amended

on _____ (if applicable).

☒ was filed as PCT international application

Number PCT/FR00/00360

on February 14, 2000

and was amended

on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims,
 as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in
 Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(e) of any foreign application(s) for
 patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the
 United States of America listed below and have also identified below any foreign application(s) for patent or inventor's
 certificate or any PCT international application(s) designating at least one country other than the United States of America
 filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. §119:

COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C. §119
France	99/02011	18 February 1999	<u>X</u> Yes <u> </u> No
			<u> </u> Yes <u> </u> No
			<u> </u> Yes <u> </u> No
			<u> </u> Yes <u> </u> No
			<u> </u> Yes <u> </u> No

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed
 below.

 (Application Number)

 (Filing Date)

 (Application Number)

 (Filing Date)

Attorney's Docket No.

022701-942

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose to the Office all information known to me to be material to the patentability as defined in Title 37, Code of Federal Regulations §1.56, which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. §120:

[illegible]

I hereby appoint the following attorneys and agent(s) to prosecute said application and to transact all business in the Patent and Trademark Office connected therewith and to file, prosecute and to transact all business in connection with international applications directed to said invention:

William L. Mathis	17,337
Robert S. Swecker	19,885
Platon N. Mandros	22,124
Benton S. Duffett, Jr.	22,030
Norman H. Stejno	22,716
Ronald L. Grudziecki	24,970
Frederick G. Michaud, Jr.	26,003
Alan E. Kopecki	25,813
Regis E. Slutter	26,999
Samuel C. Miller, III	27,360
Robert G. Mukai	28,531
George A. Hovanec, Jr.	28,223
James A. LaBarre	28,632
E. Joseph Gess	28,546
R. Danpv Huntington	27,903

Eric H. Weisblatt	30,505
James W. Peterson	26,057
Teresa Stanek Rea	30,427
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William C. Rowland	30,888
T. Gene Dillahunt	25,423
Patrick C. Keane	32,858
B. Jefferson Boggs, Jr.	32,344
William H. Benz	25,952
Peter K. Skiff	31,917
Richard J. McGrath	29,195
Matthew L. Schneider	32,814
Michael G. Savage	32,596
Gerald F. Swiss	30,113
Charles F. Wieland III	33,096

Bruce T. Wieder	33,815
Todd R. Walters	<u>34,040</u>
Ronni S. Jillions	31,979
Harold R. Brown III	<u>36,241</u>
Allen R. Baum	36,086
Brian P. O'Shaughnessy	<u>32,747</u>
Kenneth B. Leffler	36,075
Fred W. Hathaway	<u>32,236</u>
Wendi L. Weinstein	<u>34,456</u>
Mary Ann Dillahunty	<u>34,576</u>



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and:

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Address all telephone calls to: Norman H. Stepno at (703) 836-6620.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

022701-942

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD FOR PREPARING LATEX BY EMULSION (CO)POLYMERISATION OF ETHYLENICALLY

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the specification of which (check only one item below):

☐ is attached hereto.

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			<u> </u> Yes <u> </u> No
			<u> </u> Yes <u> </u> No
			<u> </u> Yes <u> </u> No
			<u> </u> Yes <u> </u> No

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONT'D)
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

022701-942

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PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. §120:

U.S. APPLICATIONS		STATUS (check one)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED

PCT APPLICATIONS DESIGNATING THE U.S.

PCT APPLICATION NO.	PCT FILING DATE	U.S. APPLICATION NUMBERS ASSIGNED (if any)		

I hereby appoint the following attorneys and agent(s) to prosecute said application and to transact all business in the Patent and Trademark Office connected therewith and to file, prosecute and to transact all business in connection with international applications directed to said invention:

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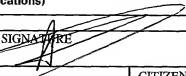
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COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONT'D)
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

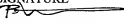
022701-942

1-00 FULL NAME OF SOLE OR FIRST INVENTOR <u>Mathias Agnely</u>		SIGNATURE 		DATE <u>Dec. 6, 2001</u>
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FULL NAME OF SEVENTH JOINT INVENTOR, IF ANY		SIGNATURE		DATE
RESIDENCE		CITIZENSHIP		
POST OFFICE ADDRESS				
FULL NAME OF EIGHTH JOINT INVENTOR, IF ANY		SIGNATURE		DATE
RESIDENCE		CITIZENSHIP		
POST OFFICE ADDRESS				

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONT'D)
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

022701-942

FULL NAME OF SOLE OR FIRST INVENTOR Mathias Agnely		SIGNATURE	DATE
RESIDENCE 9, rue de Rungis, F-75013 Paris, FRANCE		CITIZENSHIP FR	
POST OFFICE ADDRESS 9, rue de Rungis, F-75013 Paris, FRANCE			
FULL NAME OF SECOND JOINT INVENTOR, IF ANY Bruno Amram		SIGNATURE 	DATE 15 Dec 2001
RESIDENCE 69, avenue Danielle Casanova, Bâtiment B, F-94200 Ivry-sur-Seine, FRANCE		CITIZENSHIP FR FRX	
POST OFFICE ADDRESS 69, avenue Danielle Casanova, Bâtiment B, F-94200 Ivry-sur-Seine, FRANCE			
FULL NAME OF THIRD JOINT INVENTOR, IF ANY Phil D. Armitage		SIGNATURE	DATE
RESIDENCE 9 Bromley Road, Shipley, Bradford BD18 4DS, Great Britain		CITIZENSHIP GB	
POST OFFICE ADDRESS 9 Bromley Road, Shipley, Bradford BD18 4DS, Great Britain			
FULL NAME OF FOURTH JOINT INVENTOR, IF ANY Dominique Charnot		SIGNATURE	DATE
RESIDENCE 114 Via Lago Rinconada Hills, Los Gatos, CA 95032, USA		CITIZENSHIP US	
POST OFFICE ADDRESS 114 Via Lago Rinconada Hills, Los Gatos, CA 95032, USA			
FULL NAME OF FIFTH JOINT INVENTOR, IF ANY Bruno Drochon		SIGNATURE	DATE
RESIDENCE 8, place Georges Pompidou, F-93160 Noisy-le-Grand, FRANCE		CITIZENSHIP FR	
POST OFFICE ADDRESS 8, place Georges Pompidou, F-93160 Noisy-le-Grand, FRANCE			
FULL NAME OF SIXTH JOINT INVENTOR, IF ANY Eve Pere		SIGNATURE	DATE
RESIDENCE 118, avenue du Tonkin, F-64140 Lons, FRANCE		CITIZENSHIP FR	
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FULL NAME OF SEVENTH JOINT INVENTOR, IF ANY		SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF EIGHTH JOINT INVENTOR, IF ANY		SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
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Attorney's Docket No.

022701-942

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name:

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD FOR PREPARING LATEX BY EMULSION (CO)POLYMERISATION OF ETHYLENICALLY

UNSATURATED MONOMERS, WITH DIRECT INLINE MONITORING BY RAMAN SPECTROSCOPY

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Number _____

on _____

and was amended

on _____ (if applicable).

☒ was filed as PCT international application

Number PCT/FR00/00360

on February 14, 2000

and was amended

on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

☒ I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(e) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. §119:

COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C. §119
France	99/02011	18 February 1999	<u>X</u> Yes <u> </u> No
			<u> </u> Yes <u> </u> No
			<u> </u> Yes <u> </u> No
			<u> </u> Yes <u> </u> No
			<u> </u> Yes <u> </u> No

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONT'D)
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

022701-942

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose to the Office all information known to me to be material to the patentability as defined in Title 37, Code of Federal Regulations §1.56, which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. §120:

U.S. APPLICATIONS		STATUS (check one)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED
PCT APPLICATIONS DESIGNATING THE U.S.				
PCT APPLICATION NO.	PCT FILING DATE	U.S. APPLICATION NUMBERS ASSIGNED (if any)		

I hereby appoint the following attorneys and agent(s) to prosecute said application and to transact all business in the Patent and Trademark Office connected therewith and to file, prosecute and to transact all business in connection with international applications directed to said invention:

William L. Mathis	17,337	Eric H. Weisblatt	30,505	Bruce T. Wieder	33,815
Robert S. Swecker	19,885	James W. Peterson	26,057	Todd R. Walters	34,040
Platon N. Mandros	22,124	Teresa Stanek Rea	30,427	Ronni S. Jillions	31,979
Benton S. Duffett, Jr.	22,090	Robert E. Krebs	25,885	Harold R. Brown III	36,341
Norman H. Stepno	22,716	William C. Rowland	30,888	Allen R. Baum	36,086
Ronald L. Grdzicki	24,970	T. Gene Dillahunty	25,423	Brian P. O'Shaughnessy	32,747
Frederick G. Michaud, Jr.	26,003	Patrick C. Keane	32,858	Kenneth B. Leffler	36,075
Alan E. Kopecki	25,813	B. Jefferson Boggs, Jr.	32,344	Fred W. Hathaway	32,236
Regis E. Slutter	26,999	William H. Benz	25,952	Wendi L. Weinstein	34,456
Samuel C. Miller, III	27,360	Peter K. Skiff	31,917	Mary Ann Dillahunty	34,576
Robert G. Mukai	28,531	Richard J. McGrath	29,195		
George A. Hovanec, Jr.	28,223	Matthew L. Schneider	32,814		
James A. LaBarre	28,632	Michael G. Savage	32,596		
E. Joseph Gess	28,510	Gerald F. Swiss	30,113		
R. Danny Huntington	27,903	Charles F. Wieland III	33,096		

21839

and:

Address all correspondence to:



21839

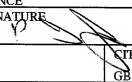
Norman H. Stepno
BURNS, DOANE, SWECKER & MATHIS, L.L.P.
P.O. Box 1404
Alexandria, Virginia 22313-1404

Address all telephone calls to: Norman H. Stepno at (703) 836-6620.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONT'D)
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.
022701-942

FULL NAME OF SOLE OR FIRST INVENTOR Mathias Agnely		SIGNATURE	DATE
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POST OFFICE ADDRESS 69, avenue Danielle Casanova, Bâtiment B, F-94200 Ivry-sur-Seine, FRANCE			
FULL NAME OF THIRD JOINT INVENTOR, IF ANY Phil D. Armitage		SIGNATURE 	DATE 10 Dec. 03
RESIDENCE 9 Bromley Road, Shipley, Bradford BD18 4DS, Great Britain		CITIZENSHIP GB	
POST OFFICE ADDRESS 9 Bromley Road, Shipley, Bradford BD18 4DS, Great Britain			
FULL NAME OF FOURTH JOINT INVENTOR, IF ANY Dominique Charmot		SIGNATURE	DATE
RESIDENCE 114 Via Lago Rinconada Hills, Los Gatos, CA 95032, USA		CITIZENSHIP US	
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RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			

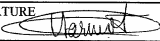
4

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (Includes Reference to Provisional and PCT International Applications)	Attorney's Docket No. 022701-942																												
<p>As a below named inventor, I hereby declare that: My residence, post office address and citizenship are as stated below next to my name; I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:</p> <p><u>METHOD FOR PREPARING LATEX BY EMULSION (CO)POLYMERISATION OF ETHYLENICALLY</u> <u>UNSATURATED MONOMERS, WITH DIRECT INLINE MONITORING BY RAMAN SPECTROSCOPY</u></p> <p>the specification of which (check only one item below):</p> <p><input type="checkbox"/> is attached hereto.</p> <p><input type="checkbox"/> was filed as United States application Number _____ on _____ and was amended on _____ (if applicable).</p> <p><input checked="" type="checkbox"/> was filed as PCT international application Number <u>PCT/FR00/00360</u> on <u>February 14, 2000</u> and was amended on _____ (if applicable).</p> <p>I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.</p> <p>I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.</p> <p>I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(e) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th colspan="4" style="text-align: left; padding: 5px;">PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. § 119:</th> </tr> <tr> <th style="width: 25%; padding: 5px;">COUNTRY (if PCT, indicate "PCT")</th> <th style="width: 25%; padding: 5px;">APPLICATION NUMBER</th> <th style="width: 25%; padding: 5px;">DATE OF FILING (day, month, year)</th> <th style="width: 25%; padding: 5px;">PRIORITY CLAIMED UNDER 35 U.S.C. § 119</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; padding: 5px;">France</td> <td style="text-align: center; padding: 5px;">99/02011</td> <td style="text-align: center; padding: 5px;">18 February 1999</td> <td style="padding: 5px;"><input checked="" type="checkbox"/> Yes <input type="checkbox"/> No</td> </tr> <tr> <td style="height: 20px;"></td> <td></td> <td></td> <td style="text-align: center; padding: 5px;"><input type="checkbox"/> Yes <input type="checkbox"/> No</td> </tr> <tr> <td style="height: 20px;"></td> <td></td> <td></td> <td style="text-align: center; padding: 5px;"><input type="checkbox"/> Yes <input type="checkbox"/> No</td> </tr> <tr> <td style="height: 20px;"></td> <td></td> <td></td> <td style="text-align: center; padding: 5px;"><input type="checkbox"/> Yes <input type="checkbox"/> No</td> </tr> <tr> <td style="height: 20px;"></td> <td></td> <td></td> <td style="text-align: center; padding: 5px;"><input type="checkbox"/> Yes <input type="checkbox"/> No</td> </tr> </tbody> </table> <p>I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.</p> <div style="display: flex; justify-content: space-between; margin-top: 10px;"> <div style="width: 45%;"> _____ (Application Number) </div> <div style="width: 45%;"> _____ (Filing Date) </div> </div> <div style="display: flex; justify-content: space-between; margin-top: 10px;"> <div style="width: 45%;"> _____ (Application Number) </div> <div style="width: 45%;"> _____ (Filing Date) </div> </div>		PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. § 119:				COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C. § 119	France	99/02011	18 February 1999	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No				<input type="checkbox"/> Yes <input type="checkbox"/> No				<input type="checkbox"/> Yes <input type="checkbox"/> No				<input type="checkbox"/> Yes <input type="checkbox"/> No				<input type="checkbox"/> Yes <input type="checkbox"/> No
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COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONT'D)
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

022701-942

FULL NAME OF SOLE OR FIRST INVENTOR <u>Mathias Agnely</u>	SIGNATURE	DATE
RESIDENCE <u>9, rue de Rungis, F-75013 Paris, FRANCE</u>	CITIZENSHIP <u>FR</u>	
POST OFFICE ADDRESS <u>9, rue de Rungis, F-75013 Paris, FRANCE</u>		
FULL NAME OF SECOND JOINT INVENTOR, IF ANY <u>Bruno Amram</u>	SIGNATURE	DATE
RESIDENCE <u>69, avenue Danielle Casanova, Bâtiment B, F-94200 Ivry-sur-Seine, FRANCE</u>	CITIZENSHIP <u>FR</u>	
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RESIDENCE <u>9 Bromley Road, Shipley, Bradford BD18 4DS, Great Britain</u>	CITIZENSHIP <u>GB</u>	
POST OFFICE ADDRESS <u>9 Bromley Road, Shipley, Bradford BD18 4DS, Great Britain</u>		
FULL NAME OF FOURTH JOINT INVENTOR, IF ANY <u>Dominique Charmot</u>	SIGNATURE 	DATE <u>12-11-01</u>
RESIDENCE <u>114 Via Lago Rinconada Hills, Los Gatos, CA 95032, USA</u>	CITIZENSHIP <u>US FR</u>	<u>CA</u>
POST OFFICE ADDRESS <u>114 Via Lago Rinconada Hills, Los Gatos, CA 95032, USA</u>		
FULL NAME OF FIFTH JOINT INVENTOR, IF ANY <u>Bruno Drochon</u>	SIGNATURE	DATE
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and: _____

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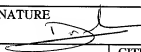
Norman H. Stepno
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FULL NAME OF FIFTH JOINT INVENTOR, IF ANY		SIGNATURE	DATE
Bruno Drochon			December 10 2001
RESIDENCE		CITIZENSHIP	
18, place Georges Pompidou, F-93160 Noisy-le-Grand, FRANCE		FR FRX	
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18, place Georges Pompidou, F-93160 Noisy-le-Grand, FRANCE			
FULL NAME OF SIXTH JOINT INVENTOR, IF ANY		SIGNATURE	DATE
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FULL NAME OF SEVENTH JOINT INVENTOR, IF ANY		SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF EIGHTH JOINT INVENTOR, IF ANY		SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			

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COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
 (Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

022701-942

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD FOR PREPARING LATEX BY EMULSION (CO)POLYMERISATION OF ETHYLENICALLY

UNSATURATED MONOMERS, WITH DIRECT INLINE MONITORING BY RAMAN SPECTROSCOPY

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Number _____

on _____

and was amended

on _____ (if applicable).

☒ was filed as PCT international application

Number PCT/FR00/00360

on February 14, 2000

and was amended

on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(e) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. § 119:

COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 U.S.C. § 119
France	99/02011	18 February 1999	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No
			<input type="checkbox"/> Yes <input type="checkbox"/> No

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONT'D)
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

022701-942

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose to the Office all information known to me to be material to the patentability as defined in Title 37, Code of Federal Regulations §1.56, which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. §120:

U.S. APPLICATIONS		STATUS (check one)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED
PCT APPLICATIONS DESIGNATING THE U.S.				
PCT APPLICATION NO.	PCT FILING DATE	U.S. APPLICATION NUMBERS ASSIGNED (if any)		

I hereby appoint the following attorneys and agent(s) to prosecute said application and to transact all business in the Patent and Trademark Office connected therewith and to file, prosecute and to transact all business in connection with international applications directed to said invention:

William L. Mathis	17,337	Eric H. Weisblatt	30,505	Bruce T. Wieder	33,815
Robert S. Swecker	19,885	James W. Peterson	26,057	Todd R. Walters	34,040
Platon N. Mandros	22,124	Teresa Sianek Rea	30,427	Ronni S. Jillions	31,979
Benton S. Duffett, Jr.	22,030	Robert E. Krebs	25,885	Harold R. Brown III	36,341
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Alan E. Kopecki	25,813	B. Jefferson Boggs, Jr.	32,344	Fred W. Hathaway	32,236
Regis E. Slitter	26,999	William H. Benz	25,952	Wendi L. Weinstein	34,456
Samuel C. Miller, III	27,360	Peter K. Skiff	31,917	Mary Ann Dillahunty	34,576
Robert G. Mukai	28,531	Richard J. McGrath	29,195		
George A. Hovanec, Jr.	28,223	Matthew L. Schneider	32,814		
James A. LaBarre	28,632	Michael G. Savage	32,596		
E. Joseph Gess	28,510	Gerald F. Swiss	30,113		
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONT'D) (Includes Reference to Provisional and PCT International Applications)	Attorney's Docket No. 022701-942
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FULL NAME OF SEVENTH JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		
FULL NAME OF EIGHTH JOINT INVENTOR, IF ANY	SIGNATURE	DATE
RESIDENCE	CITIZENSHIP	
POST OFFICE ADDRESS		